

# Inorganic chemistry

*Lecturer • 10*

Polarity of Molecules

The "charge distribution" of a molecule is determined by

- The *shape* of the molecule
- The *polarity* of its bonds

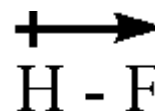
A *Polar* Molecule:

- The center of the overall negative charge on the molecule does not coincide with the center of overall positive charge on the molecule
- The molecule can be oriented such that one end has a net negative charge and the other a net positive charge, i.e. the molecule is a *dipole*

A *Nonpolar* molecule

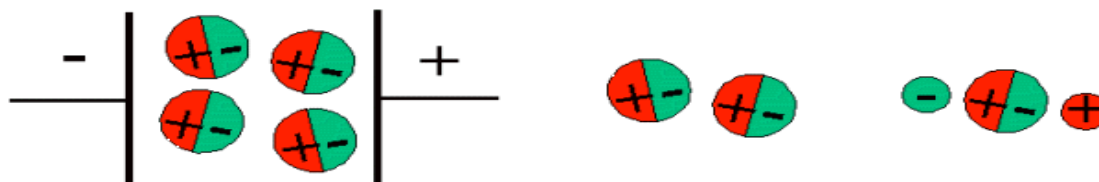
- Has no charges on the opposite ends of the molecule
- Or, has charges of the *same sign* on the opposite ends of the molecule
- Molecule is *not* a dipole

Any diatomic molecule with a polar bond is a polar molecule (dipole)



Polar molecules align themselves:

- in an electric field
- with respect to one another
- with respect to ions



The degree of polarity of a molecule is described by its *dipole moment*,  $m = Q \cdot r$

where

- $Q$  equals the charge on either end of the dipole
- $r$  is the distance between the charges

*the greater the distance or the higher the charge, the greater the magnitude of the dipole*

Dipole moments are generally reported in Debye units

$$1 \text{ debye} = 3.33 \times 10^{-30} \text{ coulomb meters (C m)}$$

**Example: H-Cl a covalent polar compound**

- The H-Cl bond distance is  $1.27\text{\AA}$
- +1 and -1 charges in a dipole produce  $1.60 \times 10^{-19} \text{ C}$

$$m = Qr = (1.60 \times 10^{-19} \text{ C})(1.27 \times 10^{-10} \text{ m})$$

$$m = 2.03 \times 10^{-29} \text{ C m}$$

$$m = 2.03 \times 10^{-29} \text{ C m} (1 \text{ debye}/3.33 \times 10^{-30}) = 6.10 \text{ debye}$$

*The actual dipole of H-Cl is 1.08 debye. The reason for this is that the compound is covalent and not ionic, thus the charges of the dipole are less than +1, and -1 (values expected for a fully ionic compound)*

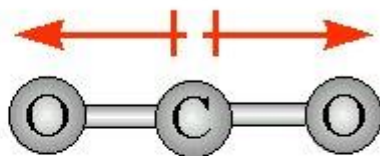
Compound	Bond Length ( $\text{\AA}$ )	Electronegativity	Dipole Moment (D)
		Difference	
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

Although the bond length is *increasing*, the dipole is *decreasing* as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the *charge* at the ends of the dipole).

**The Polarity of Polyatomic Molecules**

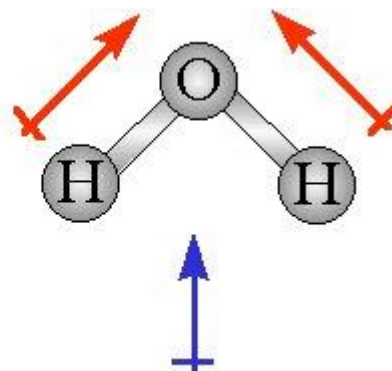
- Each polar bond in a polyatomic molecule will have an associated dipole
- The overall dipole of the molecule will be the sum of the individual dipoles

Dipoles



Overall  
Dipole:

(none)

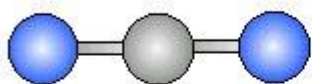


- Although in carbon dioxide the oxygens have a partial negative charge and the carbon a partial positive charge, *the molecule has no dipole* - it will not orient in an electrical field
- Water has a dipole and will orient in an electrical field

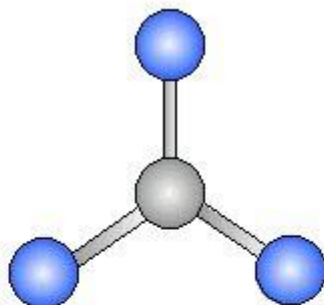
*Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

### AB<sub>n</sub> molecules and non-polar geometries

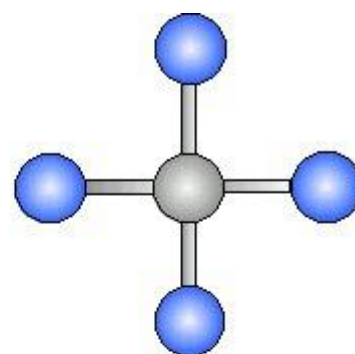
For AB<sub>n</sub> molecules, where the central atom A is surrounded by identical atoms for B, there are certain molecular geometries which result in *no effective dipole*, regardless of how polar the individual bonds may be. These geometries are:



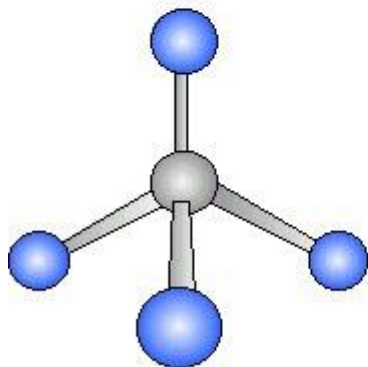
Linear



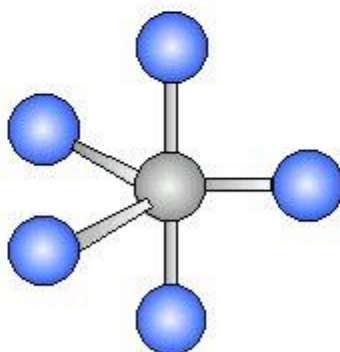
Trigonal Planar



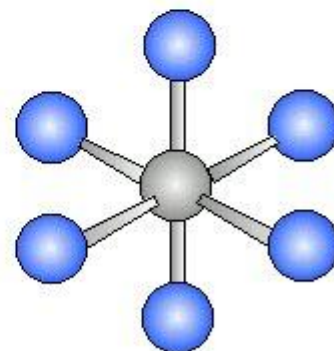
Square Planar



Tetrahedral



Trigonal Bipyramidal



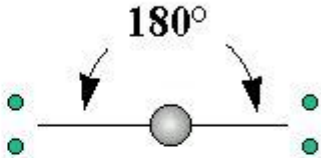
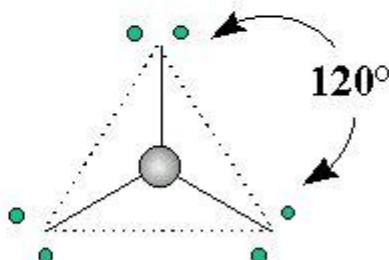
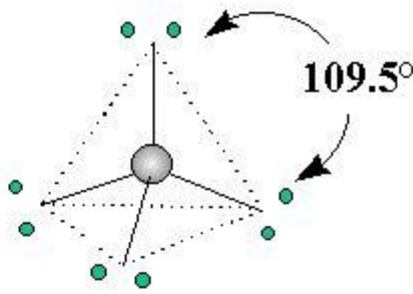
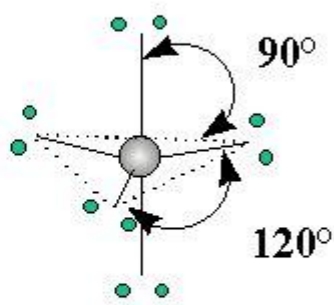
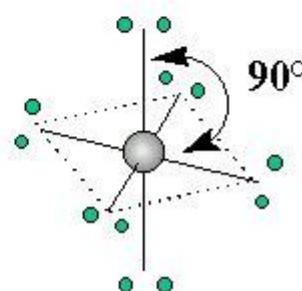
Octahedral

### Covalent Bonding and Orbital Overlap

- The VSEPR model is a simple method which allows us to predict molecular geometries, but it does not explain why bonds exist between atoms.
- How can we explain molecular geometries and the basis of bonding at the same time?

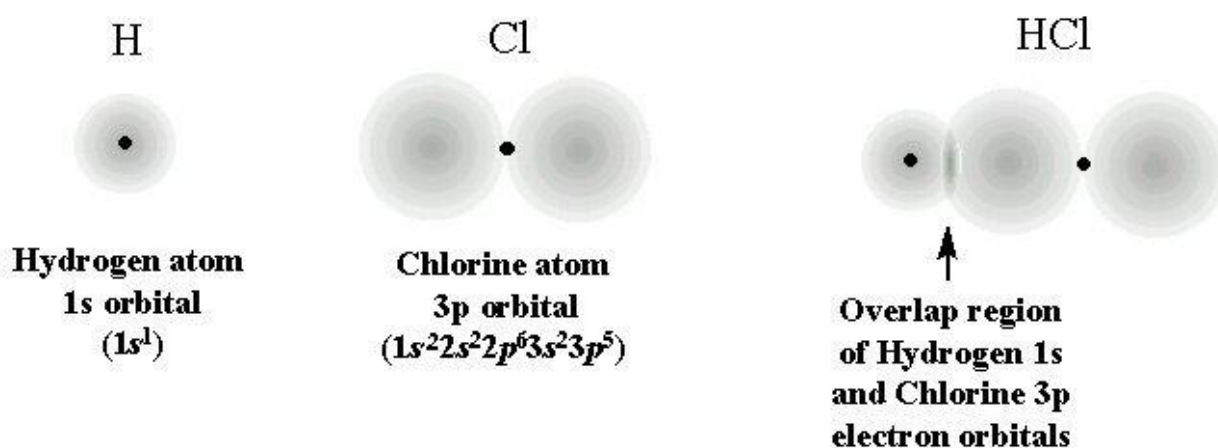
### *Quantum mechanics and molecular orbitals*

Fig.1 The shape of a molecule can be related to these five basic arrangements .

Number of electron pairs	Arrangement of electron pairs	Electron-pair geometry	Predicted bond angles
2		Linear	$180^\circ$
3		Trigonal planar	$120^\circ$
4		Tetrahedral	$109.5^\circ$
5		Trigonal bipyramid	$90^\circ$ $120^\circ$
6		Octahedral	$90^\circ$

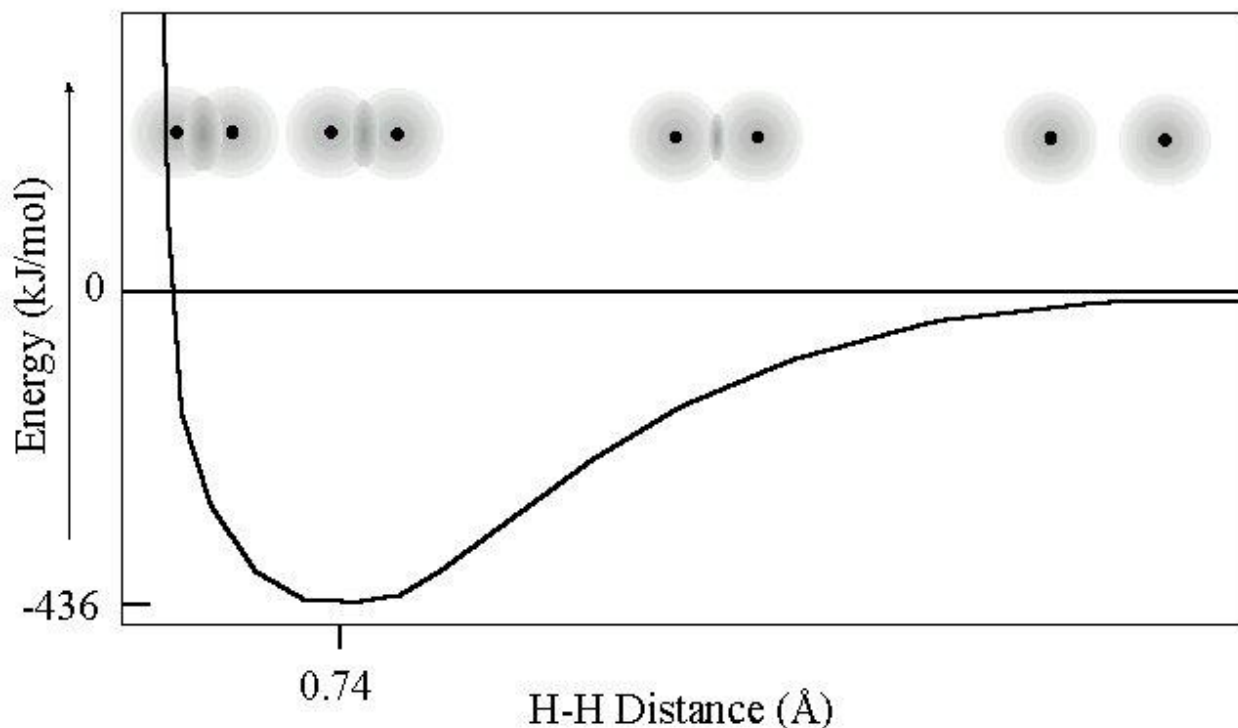
Valence bond theory

- Combine Lewis' idea of electron pair bonds with electron orbitals (quantum mechanics)
- Covalent bonding occurs when atoms share electrons (Lewis model)
- Concentrates electron density between nuclei
- The buildup of electron density between two nuclei occurs when a valence atomic orbital of one atom merges with that of another atom (Valence bond theory)
  - The orbitals share a region of space, i.e. *they overlap*
  - *The overlap of orbitals allows two electrons of opposite spin to share the common space between the nuclei, forming a covalent bond*



There is an optimum distance between two bonded nuclei in covalent bonds:

Potential Energy in Formation of  $H_2$  Bond



Important points

- As the 1s orbitals of the hydrogen start to overlap there is a reduction in the potential energy of the system (due to the increase in electron density between the two positively charged nuclei)
- As the distance decreases further, repulsion between the nuclei becomes significant at short distances
- The internuclear distance at the minimum potential energy corresponds to the observed bond length

Therefore:

*The observed bond length is the distance at which the attractive forces (nuclei for bonding electrons) is balance by the repulsive force (nuclei vs. nuclei; and additionally, electron vs. electron)*

Molecular Geometry and Bonding TheoriesHybrid Orbitals

For polyatomic molecules we would like to be able to explain:

- The number of bonds formed
- Their geometries

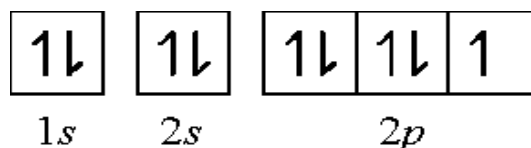
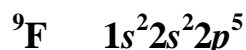
sp Hybrid Orbitals

Consider the Lewis structure of gaseous molecules of  $\text{BeF}_2$ :



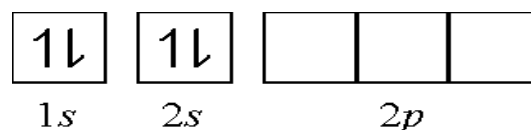
- The VSEPR model predicts this structure will be linear
- What would valence bond theory predict about the structure?

The fluorine atom electron configuration:



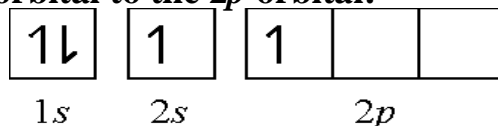
- There is an unpaired electron in a  $2p$  orbital
- This unpaired  $2p$  electron can be paired with an unpaired electron in the Be atom to form a covalent bond

The Be atom electron configuration:



- In the ground state, there are no unpaired electrons (the Be atom is incapable of forming a covalent bond with a fluorine atom)

- However, the Be atom could obtain an unpaired electron by promoting an electron from the 2s orbital to the 2p orbital:

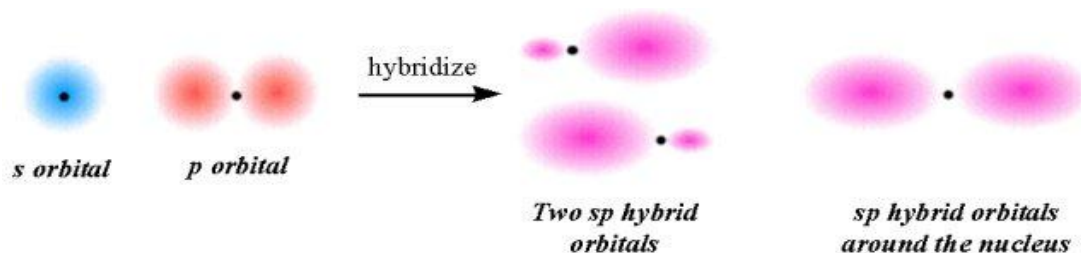


This would actually result in two unpaired electrons, one in a 2s orbital and another in a 2p orbital

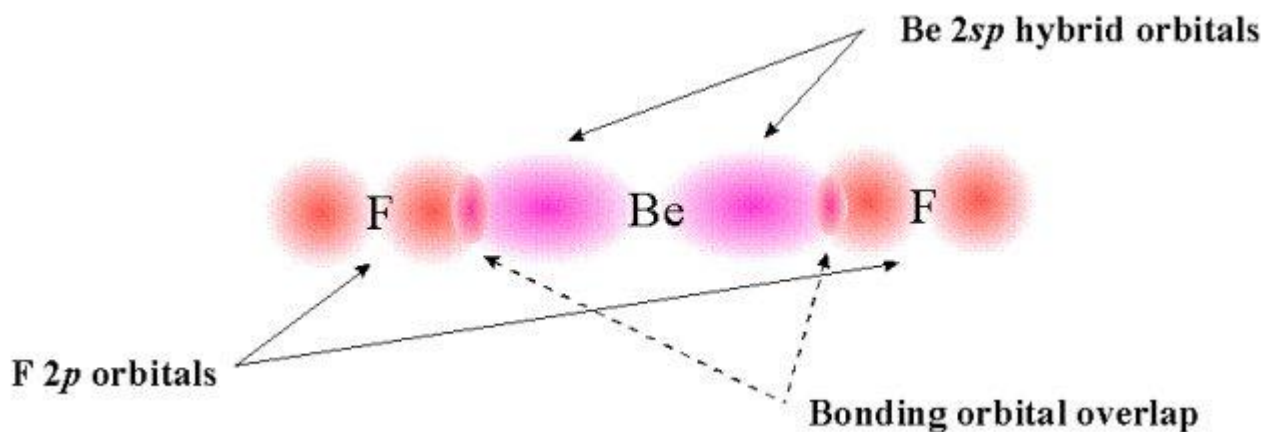
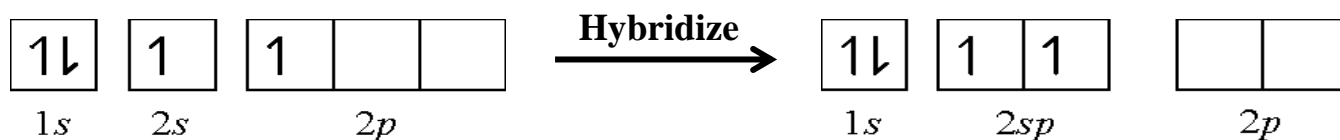
- The Be atom can now form two covalent bonds with fluorine atoms
- We would not expect these bonds to be identical (one is with a 2s electron orbital, the other is with a 2p electron orbital)

*However, the structure of  $\text{BeF}_2$  is linear and the bond lengths are identical*

- We can *combine* wavefunctions for the 2s and 2p electrons to produce a "hybrid" orbital for both electrons
- This hybrid orbital is an "sp" hybrid orbital



- The orbital diagram for this hybridization would be represented as:





**Note:**

- The Be  $2sp$  orbitals are identical and oriented  $180^\circ$  from one another (i.e. bond lengths will be identical and the molecule linear)
- The promotion of a Be  $2s$  electron to a  $2p$  orbital to allow  $sp$  hybrid orbital formation *requires energy*.
  - The elongated  $sp$  hybrid orbitals have one large lobe which can overlap (bond) with another atom more effectively
  - This produces a stronger bond (higher bond energy) which offsets the energy required to promote the  $2s$  electron

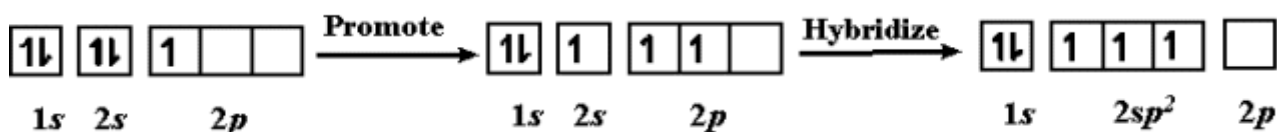
 $sp^2$  and  $sp^3$  Hybrid Orbitals

Whenever orbitals are mixed (hybridized):

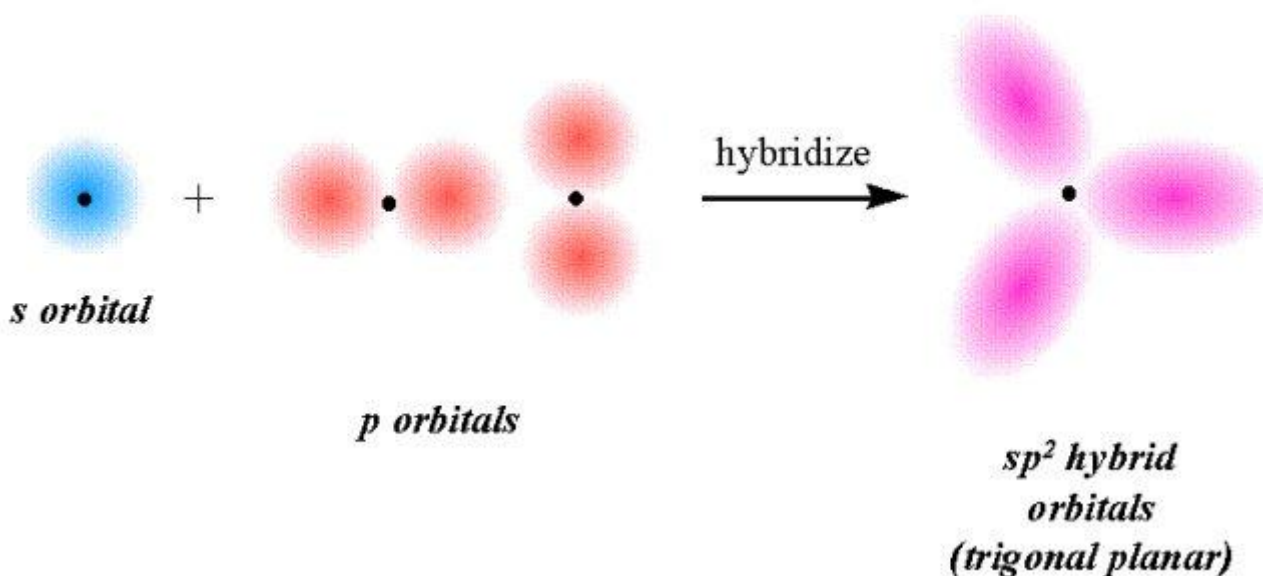
- The number of hybrid orbitals produced *is equal to the sum of the orbitals being hybridized*
- Each hybrid orbital is identical *except that they are oriented in different directions*

**BF<sub>3</sub>**

Boron electron configuration:



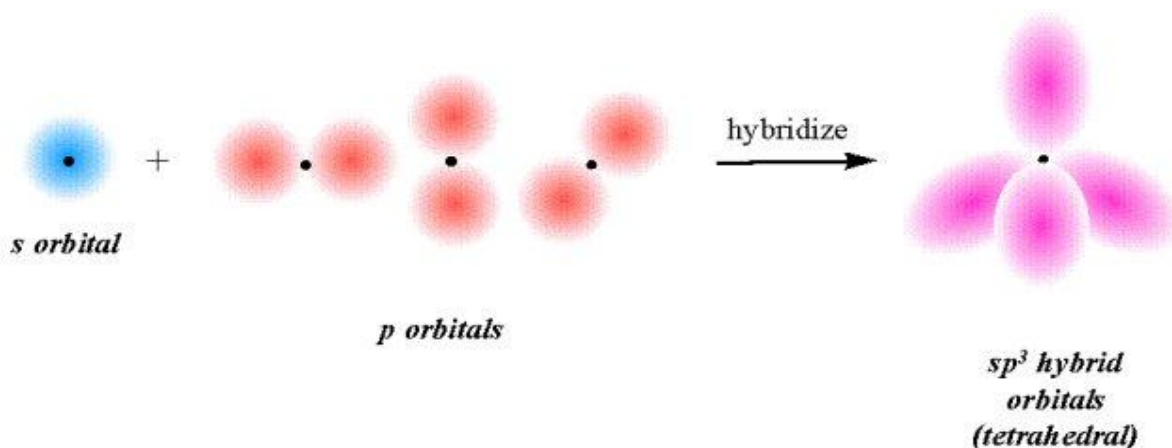
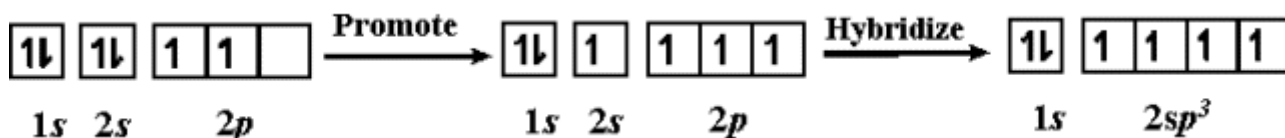
- The three  $sp^2$  hybrid orbitals have a trigonal planar arrangement to minimize electron repulsion



**NOTE:**  $sp^2$  refers to a *hybrid orbital* being constructed from one  $s$  orbital and two  $p$  orbitals. Although it looks like an electron configuration notation, the superscript '2' DOES NOT refer to the number of electrons in an orbital.

- An  $s$  orbital can also mix with all 3  $p$  orbitals in the same subshell

**CH<sub>4</sub>**

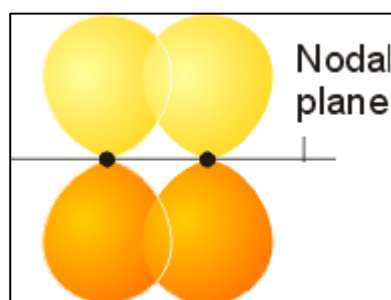
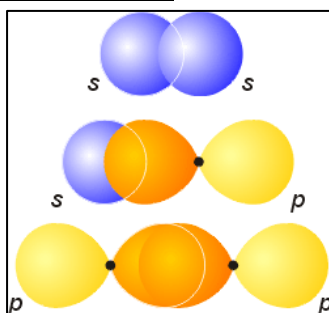


- Thus, using valence bond theory, we would describe the bonds in methane as follows: each of the carbon  $sp^3$  hybrid orbitals can overlap with the  $1s$  orbitals of a hydrogen atom to form a bonding pair of electrons

**NOTE:**  $sp^3$  refers to a *hybrid orbital* being constructed from one  $s$  orbital and three  $p$  orbitals. Although it looks like an electron configuration notation, the superscript '3' DOES NOT refer to the number of electrons in an orbital.

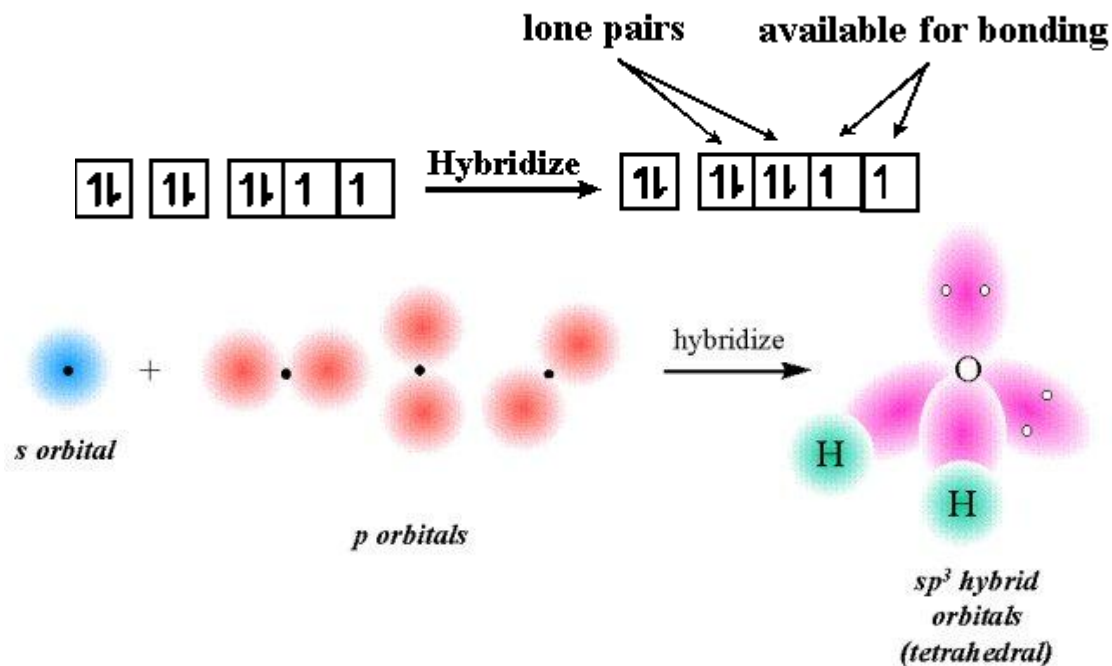
**ANOTHER NOTE:** the two steps often observed when constructing hybrid orbitals is to 1) promote a valence electron from the ground state configuration to a higher energy orbital, and then 2) hybridize the appropriate valence electron orbitals to achieve the desired valence electron geometry (i.e. the correct number of hybrid orbitals for the appropriate valence electron geometry)

### Sigma and Pi bonding



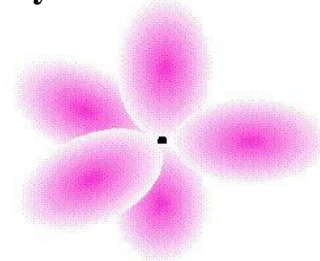
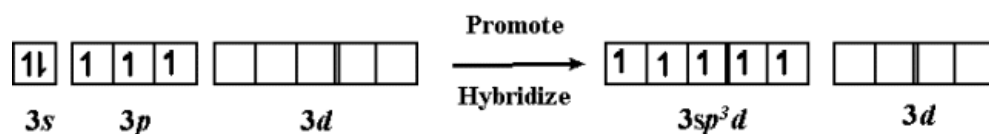


Oxygen



### Hybridization Involving $d$ Orbitals

Atoms in the third period and higher can utilize  $d$  orbitals to form hybrid orbitals



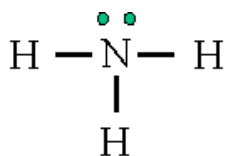
Trigonal Bipyramidal

Similarly hybridizing ones, three  $p$  and two  $d$  orbitals yields six identical hybrid  $sp^3d^2$  orbitals. These would be oriented in an *octahedral geometry*.

- Hybrid orbitals allows us to use valence bond theory to describe covalent bonds (sharing of electrons in overlapping orbitals of two atoms)
- When we know the molecular geometry, we can use the concept of hybridization to describe the electronic orbitals used by the central atom in bonding

### Steps in predicting the hybrid orbitals used by an atom in bonding:

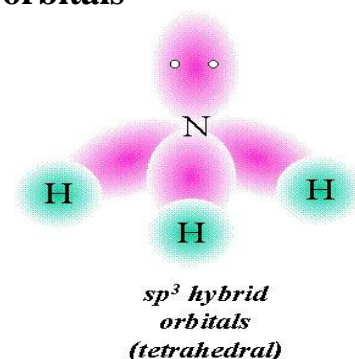
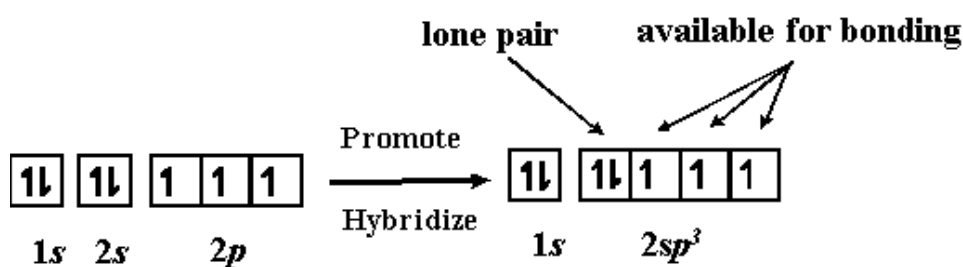
1. Draw the Lewis structure
2. Determine the electron pair geometry using the VSEPR model
3. Specify the hybrid orbitals needed to accommodate the electron pairs in the geometric arrangement



1. Lewis structure

2. VSEPR indicates *tetrahedral geometry* with one non-bonding pair of electrons (structure itself will be *trigonal pyramidal*)

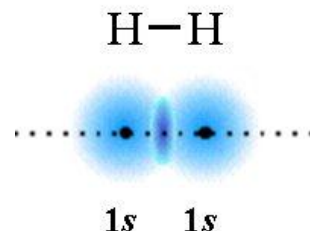
3. Tetrahedral arrangement indicates four equivalent electron orbitals



Valence Electron Pair Geometry	Number of Orbitals	Hybrid Orbitals
Linear	2	$sp$
Trigonal Planar	3	$sp^2$
Tetrahedral	4	$sp^3$
Trigonal Bipyramidal	5	$sp^3d$
Octahedral	6	$sp^3d^2$

### Multiple Bonds

The "internuclear axis" is the imaginary axis that passes through the two nuclei in a bond:

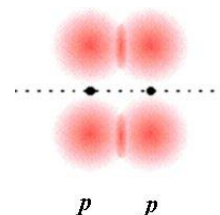


The covalent bonds we have been considering so far exhibit bonding orbitals which are *symmetrical about the internuclear axis* (either an  $s$  orbital - which is symmetric in all directions, or a  $p$  orbital that is pointing along the bond towards the other atom, or a hybrid orbital that is pointing along the axis towards the other atom)

*Bonds in which the electron density is symmetrical about the internuclear axis are termed "sigma" or " $\sigma$ " bonds*

In multiple bonds, the bonding orbitals arise from a different type arrangement:

- Multiple bonds involve the overlap between two  $p$  orbitals
- These  $p$  orbitals are oriented perpendicular to the internuclear (bond) axis



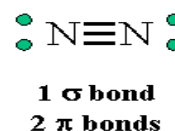
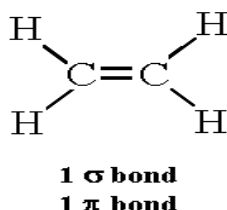
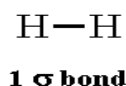
*This type of overlap of two p orbitals is called a "pi" or " $\pi$ " bond. Note that this is a single  $\pi$  bond (which is made up of the overlap of two p orbitals)*

### In $\pi$ bonds:

- The overlapping regions of the bonding orbitals lie *above* and *below* the internuclear axis (there is no probability of finding the electron in that region)
- The size of the overlap is smaller than a  $\sigma$  bond, and thus the bond strength is typically less than that of a  $\sigma$  bond

### Generally speaking:

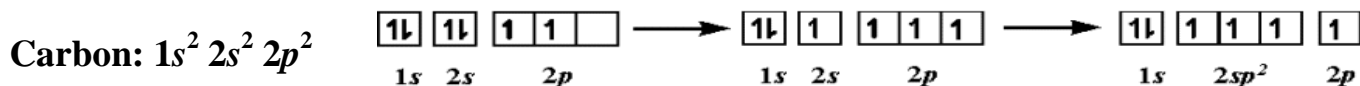
- A single bond is composed of a  $\sigma$  bond
- A double bond is composed of *one*  $\sigma$  bond and *one*  $\pi$  bond
- A triple bond is composed of *one*  $\sigma$  bond and *two*  $\pi$  bonds



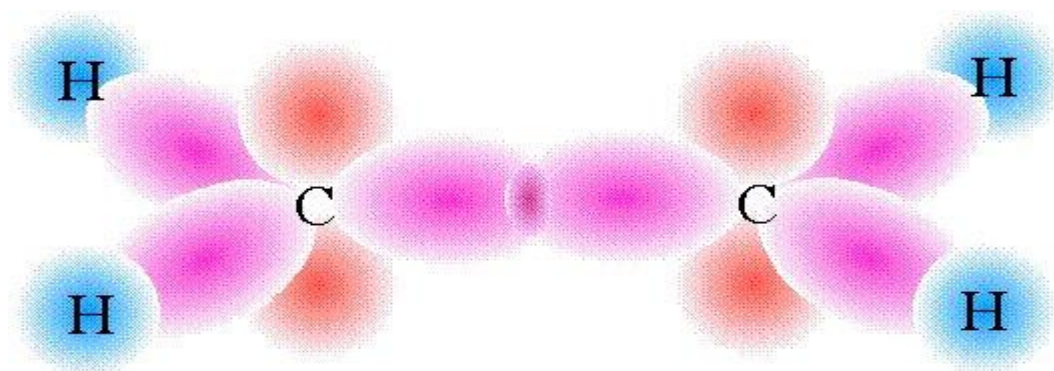
**C<sub>2</sub>H<sub>4</sub>** (ethylene; see structure above)

- The arrangement of bonds suggests that the geometry of the bonds around each carbon is *trigonal planar*
- Trigonal planar suggests  $sp^2$  hybrid orbitals are being used (these would be  $\sigma$  bonds)

What about the electron configuration?

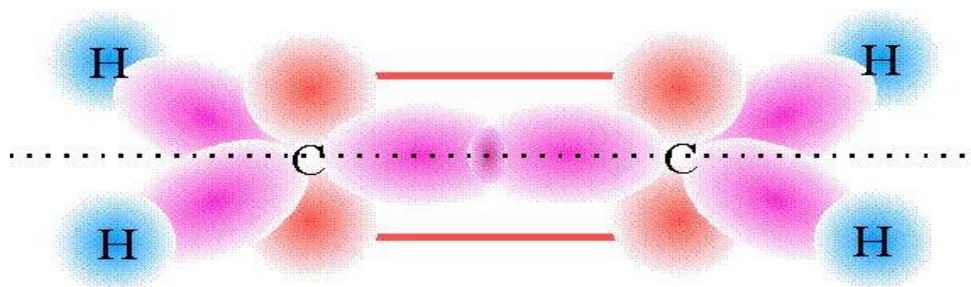


- Thus, we have an extra unpaired electron in a p orbital available for bonding
- This extra p electron orbital is oriented perpendicular to the plane of the three  $sp^2$  orbitals (to minimize repulsion):





- The unpaired electrons in the  $p$  orbitals can overlap one another above and below the internuclear axis to form a covalent bond



- This interaction above and below the internuclear axis represents the *single*  $\pi$  bond between the two  $p$  orbitals

### Experimentally:

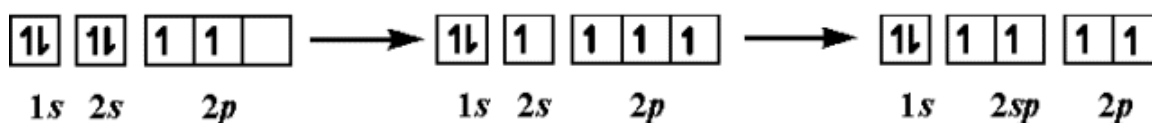
- we know that the 6 atoms of ethylene lie in the same plane.
- If there was a single  $\sigma$  bond between the two carbons, there would be nothing stopping the atoms from rotating around the C-C bond.
- But, the atoms are held rigid in a planar orientation.
- This orientation allows the overlap of the two  $p$  orbitals, with formation of a  $\pi$  bond.
- In addition to this rigidity, the C-C bond length is shorter than that expected for a single bond.
- Thus, extra electrons (from the  $\pi$  bond) must be situated between the two C-C nuclei.



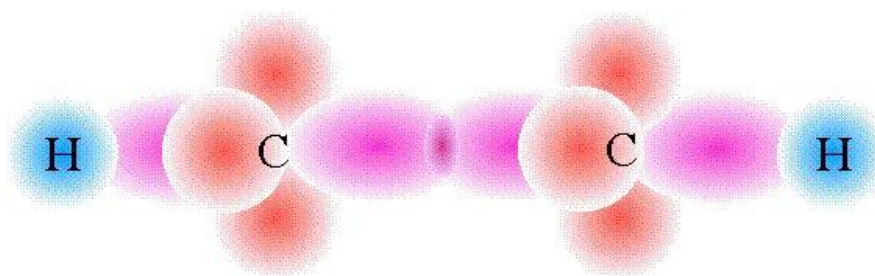
(acetylene)



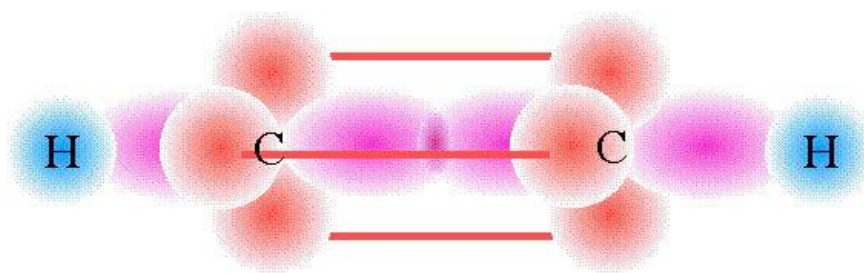
- The linear bond arrangement suggests that the carbon atoms are utilizing  $sp$  hybrid orbitals for bonding



- This leaves two unpaired electrons in  $p$  orbitals
- To minimize electron repulsion, these  $p$  orbitals are at right angles to each other, and to the internuclear axis:



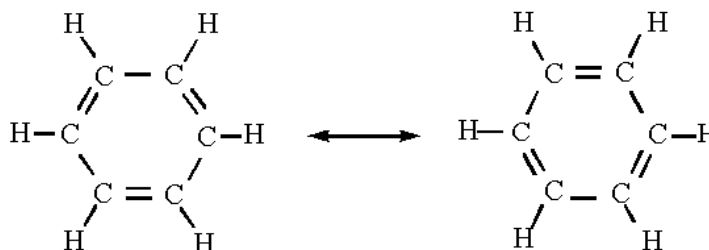
- These  $p$  orbitals can overlap two form two  $\pi$  bonds in addition to the single  $\sigma$  bond (forming a triple bond)



### Delocalized Bonding

*localized electrons* are electrons which are associated completely with the atoms forming the bond in question

In some molecules, particularly with resonance structures, we cannot associate bonding electrons with specific atoms

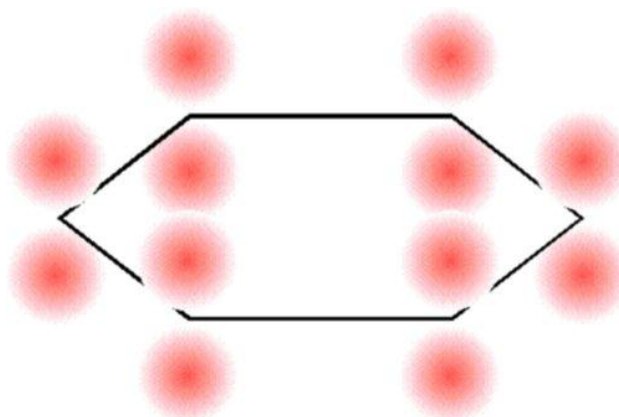


Benzene has two resonance forms

- The six carbon - carbon bonds are of equal length, intermediate between a single bond and double bond
- The molecule is planar
- The bond angle around each carbon is approximately  $120^\circ$

The apparent hybridization orbital consistent with the geometry would be  $sp^2$  (trigonal planar arrangement)

- This would leave a single  $p$  orbital associated with each carbon (perpendicular to the plane of the ring)



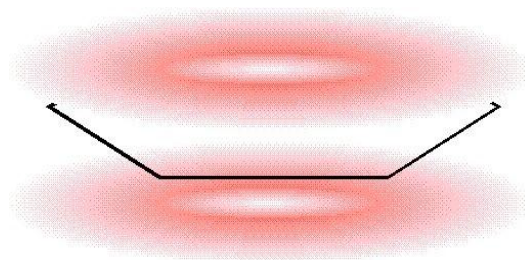
With six  $p$  electrons we could form three discrete  $\pi$  bonds

- However, this would result in three double bonds in the ring, and three single bonds
- This would cause the bond lengths to be different around the ring (which they are not)
- This would also result in one resonance structure being the only possible structure

The best model is one in which the  $\pi$  electrons are

"smeared" around the ring, and not localized

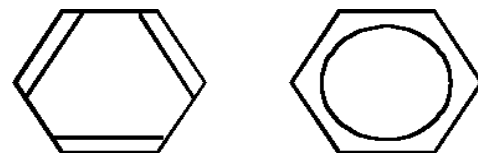
to a particular atom



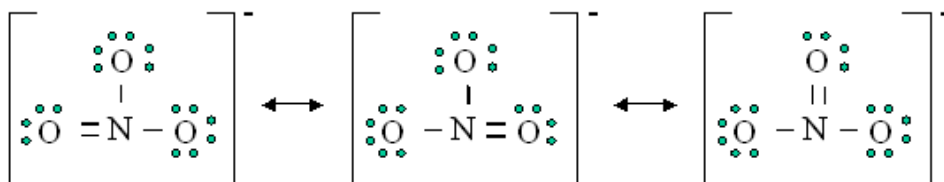
- Because we cannot say that the electrons in the  $\pi$  bonds are localized to a particular atom they are described as being *delocalized* among the six carbon atoms

Benzene is typically drawn in two different ways:

- The circle indicates the delocalization of the  $p$  bonds



### Structure of $\text{NO}_3^-$



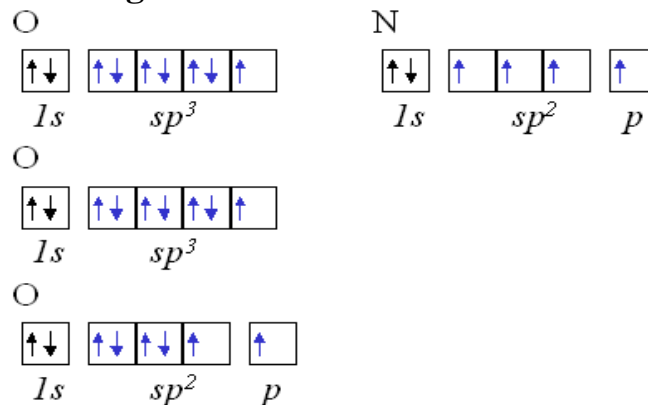
The Lewis structure of  $\text{NO}_3^-$  ion suggests that three resonance structures describe the molecular structure

- For any individual Lewis resonance structure the electronic structure for the central N atom is predicted to be  $sp^2$  hybrid orbitals participating in  $\sigma$  bonds with each of the O atoms, and an electron in a  $p$  orbital participating in a  $\pi$  bond with one oxygen (forming a double bond)
- Two of the O atoms are predicted to have  $sp^3$  hybrid orbitals, with one orbital participating in a  $\sigma$  bond with the central N atom and the other orbitals filled with non-bonding electron pairs. The other O atom is predicted to have  $sp^2$  hybrid orbitals, with one orbital participating in a  $\sigma$  bond with the central N and two orbitals filled with non-bonding pairs of electrons. Furthermore, this last O atom is participating in a double bond with the central N atom and therefore should have an electron in a  $p$  orbital to participate in a  $\pi$  bond with the central N



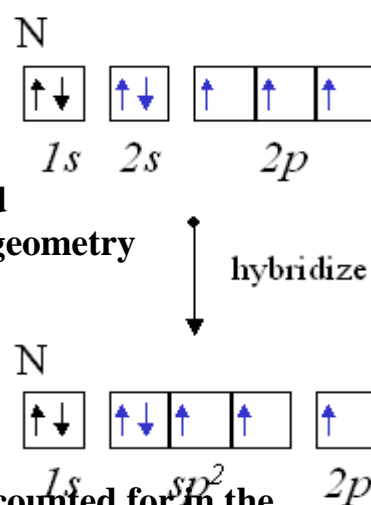
How will this arrangement look as far as the orbital diagrams?

- There are 24 valence electrons in the expected valence orbitals above
- Summing the valence electrons from the formula gives: (3 x 6) for O, plus 5 for N, plus 1 for ionic charge = 24



What might we expect for the electron configuration if we just started with the N atom?

- We would predict that the N can only make two  $\sigma$  bonds, it would have one pair of non-bonding electrons, and a  $p$  electron left over to participate in a  $\pi$  bond with one of the  $\sigma$  bonds
- This is different from what the Lewis structure shows, and from our prediction of hybrid orbitals from the expected geometry
- If we look at the  $sp^3$  O atoms above we see that they actually have 7 electrons (1 *more* than expected), while the  $sp^2$  O atom has the expected 6. Furthermore, the N atom (in the correct  $sp^2$  configuration) has 4 electrons (1 *less* than expected)
- The "extra" electron from the ionic charge is correctly accounted for in the summation of electrons



Thus, the correct way to determine electron configurations appears to be:

- begin by predicting the hybridization orbitals
- then determine lone pair arrangements and  $s$  and  $p$  bonding electrons for each atom
- confirm that all bonding electrons are correct and that the total of electrons is correct

##### حصري #####

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